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APPARATUS FOR A FUEL PROCESSING SYSTEM

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Title: Apparatus for a fuel processing system

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Background to the technology:

Field

The present invention relates to new apparatuses useful for the conversion by steam reforming of hydrocarbons and fossil fuels into hydrogen that is the feedstock for fuel cell stacks that generate electricity. Still more particularly, the present invention is concerned with particular equipment, a hydrocarbon generating apparatus, a single vessel heat integrated multi-stage water-gas shift reactor, a multiple heat source boiler, a multifunctional heat exchanger, and a multi-staged preferential oxidation reactor, and the combination thereof into a fuel processor. The present invention is further related to the integration of said fuel processor with a fuel cell stack.

Description of the prior art

Distributed electrical power systems for residences can be realized by the combination and integration of various equipment. This invention relates to improvements in specific fuel processing equipment used to produce hydrogen for a fuel cell stack and more particular to the synergies that can be obtained from specific methods of combination and integration of said fuel cell stack operating on hydrogen with said fuel processing equipment that produces the required hydrogen, to form systems that are suitable for residential distributed power generation.

However means of improving fuel processing apparatuses are continually being sought, and as a consequence many patents have issued in this area.

U.S. Pat. No. 4847051 claims a fuel processor in a fuel cell power plant. It describes the advantages of sleeves about the individual catalyst tubes within the reformer. It does not suggest any particular technique for combining the reformer with the fuel cell.

U.S. Pat. No.4650727 discloses a fuel cell power system combining a fuel cell and a fuel processing apparatus that operates on an organic fuel such as methanol using a fuel conversion catalyst specifically identified as a partially reduced copper oxide and zinc oxide solid. Although this catalyst has frequently been used for methanol conversion, it is well known that other catalysts are superior to it for steam reforming fuel feed stocks other than methanol. Since systems to distribute methanol to residences are not generally available whereas distribution systems are in place for fuels such as natural gas and

liquefied petroleum gas, methanol is unlikely to be a fuel for residential power generation.

U.S. Pat. No. 5985474 discloses a combination of a fuel cell and a furnace that are heated with a hydrogen containing reformate produced by a fuel processor or reformer, in order to provide both electricity and heat to a residence. Although it is essential to use a hydrogen containing feedstock as the fuel for the fuel cell, there are other possibilities for the fuel used in furnaces. It is much more efficient to use a fuel such as natural gas or liquefied petroleum gas directly in a furnace than to use energy to convert that fuel to a hydrogen containing reformate and subsequently burn the hydrogen containing reformate in the furnace.

U.S. Pat. No. 5401589 discloses a combination of a fuel cell and a reformer to generate electrical power. For example, waste gases were fed to a turbine to generate electricity. The various components in the systems functioned independently of one another. Any integration of the fuel cell with the fuel processor was limited.

It is the object of the present invention to provide an improved fuel processing apparatus comprised of a hydrogen generating apparatus, a single vessel heat integrated multi-stage water-gas shift reactor, a multifunctional heat exchanger, a multiple source boiler, and a single vessel water heat exchanged multi-staged preferential oxidation reactor, that when combined to form a fuel processing apparatus satisfy the criteria of compact size for residential application, short start-up times that are consistent with residential needs, rapid responses to transient changes in demand for electricity, and maximum energy efficiency. It is a further object of the present invention to integrate a fuel cell stack with the said fuel processing apparatus by multiple means.

It is a further object of the present invention to provide various embodiments of a fuel processor apparatus having the aforesaid characteristics, including methods of further improvement by operating the fuel processing apparatus with a fuel cell stack in a manner whereby integration is performed by more that one means simultaneously to achieve various advantageous results.

The present invention will be best understood, and further objects and advantages thereof will be apparent, from the following description when read in connection with the accompanying drawings.

Summary of the invention:

Improvements over the prior art are provided according to the present invention by first improving each major equipment sub-system of the fuel processor. According to the present invention the hydrogen generating apparatus is equipped with a side mounted metal fiber burner that operates in a blue flame mode that is located just above the burner surface producing heat in a convective way. The single vessel heat-integrated multi-stage water-gas shift reactors combine two or more water-gas shift reactors within a single vessel having means of communicating with a multi-functional heat exchanger that

decreases the temperature of the process gas from the high temperature shift reactor to a desired value while simultaneously transferring the unwanted heat to water that is re-circulated to a boiler for the generation of steam. The multi-functional heat exchanger not only transfers heat from the process gas from the high temperature water gas shift reactor, it also contains an immersion electrical heater that can transfer heat via re-circulated water to produce steam. The immersion water heater is particularly important for rapid start-up when the system has not been used for an extended period. The multiple heat source boiler obtains heat from the process gas from the high temperature water-gas reactor and from the electrical immersion heater as described above. In addition heat is received from the process gas from the low temperature shift reactor and from the combustion gas mixture from the combustion chamber. The single vessel water exchanged multi-stage preferential oxidation reactor is divided into at least two stages. Make-up air is added to each of the stages, thereby providing an improved distribution of air and ensuring that not all the air is used in the first part of the reactor. Each preferential oxidation reactor stage has a particular shell and tube design. In one embodiment of the present invention, warm cooling water exiting from the fuel cell stack is used on the shell side. It acts as a sink for the exothermic heat of reaction from the preferential oxidation reaction that must be managed in the first stage of the preferential oxidation reaction. It also provides a controlled temperature to ensure that an adequate rate of preferential oxidation is maintained and that the small quantities of carbon monoxide that enter the second stage are converted to obtain the 10 ppm carbon monoxide specification.

Another aspect of the present invention provides for the integration of the fuel processing apparatus with a fuel cell stack through more than one means simultaneously. As described above a first means of integrating the fuel processor with the fuel cell is through the warm cooling water exiting from said fuel cell stack that is subsequently used on a shell side of the preferential oxidation reactor. A second means of integrating the two apparatuses is by routing the anode off-gas containing un-reacted hydrogen from said fuel cell stack to the hydrogen generating apparatus within said fuel processing apparatus for burning inside the combustion chamber. A third means of integrating the two apparatuses is through the supply stream of the hydrogen containing product process gas that is made by said fuel processing apparatus and consumed by said fuel cell stack.

Brief description of drawings:

Fig. 1 is a process flow diagram illustrating the apparatus and flow paths of the fuel processing apparatus according to the present invention.
Fig. 2 is a diagram illustrating one preferred embodiment of the hydrogen generation apparatus including a combustion chamber, a burner, a steam reformer catalytic reactor, and a heat exchanger.
Fig. 3 is a diagram illustrating one preferred embodiment of the single vessel heat-integrated multi-stage water-gas shift reactor.
Fig. 4 is a diagram illustrating one preferred embodiment of the multiple heat source boiler.

Fig. 5 is a diagram illustrating one preferred embodiment of the multi-function heat exchanger.
Fig. 6 is a diagram illustrating one preferred embodiment of the single vessel water heat exchanged multi-staged preferential oxidation reactor.

Detailed description of the invention:

The apparatus and equipment for generating a hydrogen-containing gas of the quality necessary for sustained operation of a polymer electrolyte fuel cell stack is illustrated in Fig. 1, which is one embodiment of the present invention. A hydrocarbon feedstock or fossil fuel, such as natural gas, liquefied petroleum gas, diesel fuel, **1** is passed through a fixed bed of adsorbent **2**, preferably an activated carbon adsorbent or an activated carbon adsorbent impregnated with copper, wherein odorants such as mercaptans or hydrothiophenes are adsorbed to produce a hydrocarbon feedstock that is almost sulfur free; having a sulfur content less than the specification of the catalysts used to within the fuel processing apparatus to produce a hydrogen-containing gas mixture. A portion of the desulfurized hydrocarbon **3** is mixed with steam **5** to become the steam reformer catalytic reactor feedstock mixture. Another portion of the desulfurized hydrocarbon **4** is mixed with other gases and used as a combustion fuel. The steam reformer catalytic reactor feedstock mixture is heated in the feedstock pre-heat exchanger **6** by heat transferred from the steam reformer catalytic reactor product gases, **10** to become the heated steam reformer catalytic reactor gas feedstock, 7. The feedstock **7** is reacted via the steam reforming reaction to form a reformate product gas mixture, **10** comprised of carbon monoxide, hydrogen, and other gases after passing through a fixed bed of steam reforming catalyst contained in the U-tube shaped steam reformer catalytic reaction vessel, **8** that is part of the hydrogen generating apparatus, 9. A suitable steam reforming catalyst is commercially available as G-91 from Sud-Chemie. After passing through the pre-heat exchanger **6** and being cooled the cooled steam reformer catalytic reactor product gas mixture **11** enters the fixed bed of high temperature water-gas shift catalyst contained within the single vessel heat integrated multi-stage water-gas shift reactor, **12.** A suitable high temperature water-gas catalyst is available commercially as G-3 C from Sud-Chemie. The product gas mixture from the fixed bed of high temperature water-gas shift catalyst, **13** flows through multi-functional heat exchanger **14** where its temperature is decreased and it becomes the feedstock **18** to the fixed bed of low temperature water-gas shift catalyst contained within the single vessel heat integrated multi-stage water-gas shift reactor, **12.** A suitable low temperature water-gas shift catalyst is available commercially as C 18-8 from Sud-Chemie. The water-gas shift reaction of carbon monoxide with water to form an additional quantity of hydrogen plus carbon dioxide occurs within the single vessel heat integrated multi-stage water-gas shift catalysts. The product process gas from the single vessel heat integrated multi-stage water-gas shift reactor **19** flows through the inside of some of the tubes within the multiple heat source boiler **20** where the heat it transfers to the water within the multiple heat source boiler is some of the heat necessary to generate the amount of steam required for steam reforming reaction. The cooled product process gas from the multiple heat source boiler **21** passes through an air cooled heat exchanger **22** to decrease its temperature below its dew point and thereby to condense some of its water to form a vapor / liquid phase mixture, **23.**

The mixture passes into a separator vessel **24** to form a vapor stream **25** and a liquid water stream **43**. The vapor stream **24** is mixed with some of the air **27** from an air blower **26** and enters the first catalyst stage of a single vessel water heat exchanged multi-staged preferential oxidation reactor **28**. After the first stage within the single vessel water heat exchanged multi-stage preferential oxidation reactor **28**, the product process gas is mixed with the balance of air **27** from the air blower **26** and is passed through a second catalyst stage within the single vessel water-heated multi-stage preferential oxidation reactor **28**. The temperature of the catalyst stages within the single vessel water heat exchanged multi-stage preferential oxidation reactor is maintained by circulating a water stream such as the cooling water from the fuel cell stack. The product process gas from the single vessel water heat exchanged multi-stage preferential oxidation reactor **31** is the hydrogen containing feedstock gas for the fuel cell stack **32**. A portion of the hydrogen in the fuel cell stack feedstock **31** is consumed in the fuel cell stack. The portion of hydrogen that is not consumed remains in the anode off gas **33** from the fuel cell stack that is used as one of the fuels that are burned in the combustion chamber of the hydrogen generating apparatus **9** to supply the endothermic heat of the steam reforming reaction. The combustion product gas **36** from the hydrogen generating apparatus flows through the inside of some of the tubes in the multiple heat source boiler **20** where the heat that is transferred to the water is some of the heat necessary to generate the steam **5** required for the hydrogen generating apparatus. The combustion product gas **37** leaving boiler **20** transfers some of its heat in heat exchanger **38** to the boiler feed water **43** that enters boiler **20**. Domestic water **40** is treated by chlorine removal and ion exchange in a water treatment cartridge **41** to produce make-up water **42** that initially flows into the bottom of separator **24** and ultimately into boiler **20**.

The components of the equipment used in the hydrogen generating apparatus, including a combustion chamber, a burner, a steam reformer catalytic reactor, and a heat exchanger are illustrated in Fig. 2, which is one embodiment of the present invention. The hydrogen generating apparatus **9** is composed of a combustion chamber **52** that is surrounded by insulation **51**, a burner **35**, a U-tube shaped steam reforming catalytic reaction vessel **8**, and a double pipe heat exchanger **53**. The mixture of hydrocarbon and steam enter U-tube shaped steam reforming catalytic reaction vessel **8** through means **7** and are heated in double pipe heat exchanger **53**, pass through a fixed bed of steam reforming catalyst where the hydrocarbon and steam are converted to carbon monoxide and water. The steam reformer product gases exit the U-tube shaped steam reforming reactor vessel through means **10**. The endothermic heat required by the steam reforming reaction is provided by heat delivered from burner **35** by burning a mixture of hydrocarbon, anode off-gas, and air in combustion chamber **52**. The mixture of combustion gas products passes through double pipe heat exchanger **52**, transferring heat to the incoming mixture of hydrocarbon and steam and subsequently exits through means **36**.

Description of the preferred embodiment

In a preferred embodiment, the combustion chamber **52** has an internal diameter of 12 inches and an internal length of 18 inches. Each side of the U-tube shaped steam reforming reaction vessel has a length of 23 inches, measured from the exterior of the

hydrogen generating apparatus **9** to the point of maximum radius of the U portion of the U-tube. The U-tube shaped steam-reforming vessel is fabricated from a 2 inch 310 stainless steel schedule 40 pipe. A thickness of 5 inches of insulation surrounds the combustion chamber. The outer pipe of the double pipe heat exchanger is fabricated from 3 inch 304 stainless steel tubing having a 1/8 inch wall thickness. The burner is a conical shaped burner commercially available from Acotech.

The equipment used in the single vessel heat integrated multi-stage water-gas shift reactor, including two water gas shift reactors, and a means of exchanging heat with a multi-functional heat exchanger are illustrated in Fig. 3, which is one embodiment of the present invention. The reformer product gas mixture enters the single vessel heat integrated multi-stage water-gas shift reactor **12** through inlet means **11** and passes through the fixed bed of high temperature water-gas shift catalyst **61**, and exits through exit means **13** to pass to the multi-functional heat exchanger and return through entrance means **18** to flow through the fixed bed of low temperature water-gas shift catalyst **63** and exit through exit means **19**. Port **62** of the single vessel heat integrated multi-stage water-gas shift reactor **12** is used to replace the low temperature water-gas shift catalyst **63** when required.

Description of the preferred embodiment

In a preferred embodiment, the water-gas shift reaction vessel was fabricated from 4 inch 304 stainless steel schedule 40 piping. The length of the vessel was 28 inches. The inlet to the fixed bed of high temperature water-gas shift catalyst was located at the upper end of the vessel. A solid bulkhead plate was welded to form a gas tight seal at the center of the vessel. An outlet from the fixed bed of high temperature water-gas shift catalyst fabricated from ½ inch 304 stainless steel piping was centered 1 ¼ inches above the center line of the vessel. An inlet to the fixed bed of low temperature water-gas shift catalyst fabricated from ½ inch 304 stainless steel piping was centered 1 ¼ inches below the center line of the vessel. The outlet from the fixed bed of low temperature water-gas shift catalyst was located at the bottom end of the vessel.

The equipment used in the multiple heat source boiler, including a means of exchanging heat with a multi-functional heat exchanger, a means of receiving heat from the multi-functional heat exchanger, and a means of exchanger heat with the single vessel heat integrated multi-stage water-gas shift reactor are illustrated in Fig. 4, which is one embodiment of the present invention. Boiler feed water enters the multiple heat source boiler through inlet means **71**, receives heat to change its phase into steam and exits through exit means **5**. Heat is provided to the multiple heat source boiler **20** by the product process gas from the single vessel heat integrated multi-stage water-gas shift reactor **19** which flows through a first bank of 10 tubes **72** and exits through exit means **21**. A second means of receiving heat is from the combustion product gas from the combustion chamber **36** that flows through a second bank of 42 heat exchange tubes **73** and exits through exit means **37**. The third means of providing heat to the multiple heat source boiler, **20** is by re-circulating water **16** from boiler **20** to the multi-functional heat

exchanger and receiving this stream returned in the form of a water-vapor mixture through inlet means **17**.

Description of the preferred embodiment

In a preferred embodiment the multiple heat source boiler was a unique shell and tube heat exchanger fabricated from 10 inch 304 stainless steel piping. It had a length of 19 inches. A partial tube sheet was located 2 ½ inches from the end of the boiler at which the combustion gas mixture entered. Another partial tube sheet was located 3 inches from the end at which it exited. The headspace at each end where gases entered and exited various tubes was divided into two different sections. One of the sections contained 10 tubes through which the process gas flowed. The other headspace section contained 42 tubes through which the combustion gas mixture flowed. All of the tubes were ½ inch 304 stainless steel set on 5/8 inch triangular pitch. The space on the exterior of the tubes was filled with the water that was being heated to form steam.

The equipment used in the multi-functional heat exchanger having a means of exchanging heat with the multiple heat source boiler, a means of exchanger heat with the single vessel heat integrated multi-stage water-gas shift reactor, and a means of receiving heat from an electrical device are illustrated in Fig. 5, which is one embodiment of the present invention. The exit stream from the fixed bed of the high temperature water-gas shift catalyst in the single vessel heat integrated multi-stage water-gas shift reactor enters the multi-functional heat exchanger **14** through inlet means **13** passes through heat exchange tube **81** and exits through exit means **18**. The re-circulated water from the multiple heat source boiler enters through inlet means **16** passes through the shell side of the tubes in multi-functional heat exchanger **14** and exits through exit means **17** as a water-vapor mixture to return to the multiple heat source boiler. The third means of providing heat to the multi-functional heat exchanger **14** is from an electrical heating device such as an immersion electrical heater that is connected to the multi-functional heat exchanger **14** through connection **15**.

Description of the preferred embodiment

In a preferred embodiment the multi-functional heat exchanger was fabricated from 3 inch 304 stainless steel schedule 40 piping having a length of 16 inches. 304 stainless steel piping, in the form of a U enters and leaves the top of the vessel. This piping is connected to the water-gas shift reaction vessel. ½ inch fine National Pipe Thread fittings are used on the side of the heat exchanger to make connections with the water re-circulated to and from the multiple heat source boiler. A 1 inch fine National Pipe Thread connection at the bottom of the vessel is used to connect the electrical immersion water heater.

The equipment used in the single vessel water exchanged multi-staged preferential oxidation reactor is illustrated in Fig. 6, which is one embodiment of the present invention. The diagram in Fig. 6 shows an embodiment that is a preferential oxidation reactor of two stages. The product process gas mixed with air enters a first stage through

inlet means **25**, and flows through a first bank of parallel tubes, **92**, each of which contains a fixed bed of preferential oxidation catalyst. The exit gas from said first stage is combined with an additional amount of air entering through inlet means **93** to form a feed mixture to a second stage **94**, of the single vessel water heat exchanged multi-stage preferential oxidation reactor **28**, which is comprised of a second bank of parallel tubes each of which contains a fixed bed of preferential oxidation catalyst. The water used to maintain the appropriate controlled temperature within the single vessel water heat exchanged multi-stage preferential oxidation reactor, and particularly to remove the exothermic heat of the preferential oxidation reactor enters at inlet means **29** and exits at outlet means **30**. The water for maintaining the appropriate temperature is typically the cooling water that has exited from the fuel cell stack. The carbon monoxide content of the product process gas entering at inlet means **25** is typically 0.3 to 1.0 percent whereas the carbon monoxide content of the hydrogen containing fuel cell stack feedstock exiting at exit means **95** is typically less than 10 parts per million.

Description of the preferred embodiment

In a preferred embodiment the single vessel water exchanged multi-staged preferential oxidation reactor is fabricated from 5 inch 304 stainless steel schedule 40 piping, having a length of 24 inches. Tube sheets were located 3 inches from each end of the preferential oxidation reactor. Nine 5/8 inch tubes fabricated from 304 stainless steel on a 7/8 inch triangular pitch occupied one half of the cross-sectional area of the reactor and were filled with preferential oxidation catalyst to form the first stage. The inlet to the headspace for the tube sheet was a ¾ inch fine National Pipe Thread fitting located at the top of the vessel. The outlets of the nine tubes were connected to a headspace at the bottom of the reactor from which ½ inch stainless steel tubing in the shape of a U formed the outlet from the first stage and the inlet to the second stage. A ¼ inch tube was the connection used to add the second stage air to the U shaped tube connecting the first stage outlet to the second stage inlet. The second stage tubes were identical to the first stage tubes. The outlets from the nine second-stage tubes were connected to a headspace at the top of the reactor. A ¾ inch fine National Pipe Thread fitting was the outlet from the second-stage headspace.

Although only specific embodiments of the present invention have been described, numerous variations can be made in these embodiments without departing from the spirit of the invention, and all such variations that fall within the scope of the appended claims are intended to be embraced thereby.

The foregoing disclosure of this invention is not considered to be limiting since variations can be made by those skilled in the art without departing from the scope and spirit of the appended claims.

Claims

We claim: